20

25

## THAT WHICH IS CLAIMED:

1. Terminal olefin functionalized macromonomers of the formula:

H<sub>2</sub>C=CH-Z-(Q)<sub>y</sub>-poly

wherein:

Z is a C3 to C18 linear, branched or cyclic alkylene radical, optionally containing aryl or substituted aryl groups;

Q is a hydrocarbyl group derived by incorporation of a compound selected from the group consisting of conjugated dienes, alkenylsubstituted aromatic compounds and mixtures thereof:

y is a number greater than 0 to about 5; and poly comprises a polymer derived from one or more anionically polymerizable monomers.

- 2. The macromonomer of Claim 1, wherein said polymer comprises one or more anionically polymerizable monomers selected from the group consisting of olefin monomers, alkenylsubstituted aromatic monomers, polar monomers and mixtures thereof.
- 3. The macromonomer of Claim 2, wherein said anionically polymerizable monomer comprises one or more olefin monomers.
- 4. The macromonomer of Claim 3, wherein said one or more olefin monomers comprises ethylene.
  - 5. The macromonomer of Claim 3, wherein said one or more olefin monomers comprises one or more conjugated diene monomers.
- 6. The macromonomer of Claim 5, wherein said one or more conjugated diene monomers is selected from the group consisting of 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, myrcene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-pentadiene, 1,3-hexadiene, 2-methyl-1,3-hexadiene, 1,3-hexadiene, 3-methyl-1,3-heptadiene, 1,3-octadiene, 3-butyl-1,3-octadiene, 3,4-dimethyl-1,3-hexadiene, 3-n-propyl-1,3-pentadiene, 4,5-diethyl-1,3-octadiene, 2,4-diethyl-1,3-

butadiene, 2,3-di-n-propyl-1,3-butadiene, 2-methyl-3-isopropyl-1,3-butadiene, and mixtures thereof.

- 7. The macromonomer of Claim 6, wherein said one or conjugated diene monomers comprises butadiene.
- 5 8. The macromonomer of Claim 6, wherein said one or more conjugated diene monomers comprises isoprene.
  - 9. The macromonomer of Claim 5, wherein poly comprises a saturated polymer.
- The macromonomer of Claim 2, wherein said anionically polymerizable
   monomer comprises one or more alkenylsubstituted aromatic monomers.
- alkenylsubstituted aromatic monomers comprises styrene, alpha-methylstyrene, vinyltoluene, 2-vinylpyridine, 4-vinylpyridine, 1-vinylnaphthalene, 2-vinylnaphthalene, 1-alpha-methylvinylnaphthalene, 2-alpha-methylvinylnaphthalene, 1,2-diphenyl-4-methyl-1-hexene, 3-methylstyrene, 3,5-diethylstyrene, 4-tert-butylstyrene, 2-ethyl-4-benzylstyrene, 4-phenylstyrene, 4-p-tolylstyrene, 2,4-divinyltoluene, 4,5-dimethyl-1-vinylnaphthalene, and mixtures thereof.
  - 12. The macromonomer of Claim 11, wherein said one or more alkenylsubstituted aromatic monomers comprises styrene.
- 20 13. The macromonomer of Claim 12, wherein poly is saturated to form a polymer comprising vinylcyclohexane units.
  - 14. The macromonomer of Claim 13, wherein poly further comprises ethylene monomer units to form vinylcyclohexane-b-ethylene blocks.
- 15. The macromonomer of Claim 1, wherein poly comprises hydrogen at the end thereof.

15

- 16. The macromonomer of Claim 1, wherein poly comprises a functional group FG at the end thereof.
- 17. The macromonomer of Claim 16, wherein FG comprises a functional group selected from the group consisting of hydroxyl, thio, amino, carboxyl, amide, silyl, acrylate, sulfonic acid, isocyanate, and epoxide.
- 18. The macromonomer of Claim 16, wherein FG comprises -Y-W-(B- $R^4R^5R^6$ )<sub>K</sub> wherein:

Y is a C1 to C18 linear, branched or cyclic alkylene radical, optionally containing aryl or substituted aryl groups;

W is oxygen, nitrogen or sulfur;

 $(B-R^4R^5R^6)$  is a protecting group in which B is an element selected from Group IVa of the Periodic Table of the Elements; and  $R^4$ ,  $R^5$ , and  $R^6$  are each independently defined as hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, cycloalkyl and substituted cycloalkyl or  $R^6$  is optionally a - $(CR^7R^8)_{l}$ - group linking two B when k is 2, wherein  $R^7$  and  $R^8$  are each independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, cycloalkyl, and substituted cycloalkyl, and l is an integer from 1 to 7; and

k is 1 when W is oxygen or sulfur and 2 when W is nitrogen.

19. The macromonomer of Claim 16, wherein FG comprises -Y-W- $(H)_K$  20 wherein:

W is oxygen, nitrogen or sulfur;

Y is a C1 to C18 linear, branched or cyclic alkylene radical, optionally containing aryl or substituted aryl groups; and

k is 1 when W is oxygen or sulfur and 2 when W is nitrogen.

- 25 20. The macromonomer of Claim 1, wherein poly comprises an olefin group CH=CH<sub>2</sub> at the end thereof.
  - 21. The macromonomer of Claim 1, wherein poly comprises a polymer segment at the end thereof.

22. A method for making terminal olefin functionalized macromonomers, the method comprising:

anionically polymerizing one or more monomers with one or more protected functionalized initiators of the formula:

 $(R^1R^2R^3-A)-O-Z-(Q)_v-M$ ,

wherein:

5

M is an alkali metal;

Z is a C3 to C18 linear, branched or cyclic alkylene radical, optionally containing aryl or substituted aryl groups;

Q is a hydrocarbyl group derived by incorporation of a compound selected from the group consisting of conjugated dienes, alkenylsubstituted aromatic compounds and mixtures thereof;

y is a number greater than 0 to about 5; and

(A-R<sup>1</sup>R<sup>2</sup>R<sup>3</sup>) is a protecting group in which A is an element selected from Group

IVa of the Periodic Table of the Elements; and R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are each independently defined as hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, cycloalkyl and substituted cycloalkyl;

to form one or more living polymer anions of the formula  $(R^1R^2R^3-A)$ -O-Z- $(Q)_y$ -poly-M; terminating polymerization to form a polymer of the formula  $(R^1R^2R^3-A)$ -O-Z-

20 (Q)<sub>y</sub>-poly-FG, wherein FG is hydrogen or a protected or unprotected functional group; removing the protecting group (R<sup>1</sup>R<sup>2</sup>R<sup>3</sup>-A)- to liberate the hydroxy functionality to form a polymer of the formula HO-Z-(Q)<sub>y</sub>-poly-FG; and

treating said deprotected polymer under conditions sufficient to eliminate the hydroxyl group to form a polymer having a terminal olefin group of the formula  $H_2C=CH-Z-(Q)_y$ -poly-FG.

- 23. The method of Claim 22, wherein said terminating step comprises an acid quenching step.
- 24. The method of Claim 22, wherein said terminating step comprises reacting said living polymer with a functionalizing agent.

- 25. The method of Claim 24, wherein said functionalizing agent is selected from the group consisting of alkylene oxides; oxygen; sulfur; carbon dioxide; halogens; propargyl halides; alkenylhalosilanes; omega-alkenylarylhalosilanes; sulfonated compounds; amides; silicon acetals; 1,5-diazabicyclo[3.1.0]hexane; allyl halides; acryloyl and methacryloyl chloride; amines; epihalohydrins; and haloalkyl trialkoxysilanes.
- 26. The method of Claim 24, wherein said functionalizing agent is an electrophile of the structure:

$$X-Y-W-(B-R^4R^5R^6)_K$$

wherein:

5

10 X is halogen selected from chloride, bromide and iodide;

Y is a C1 to C18 linear, branched or cyclic alkylene radical, optionally containing aryl or substituted aryl groups;

W is oxygen, nitrogen or sulfur;

(B-R<sup>4</sup>R<sup>5</sup>R<sup>6</sup>) is a protecting group in which B is an element selected from Group IVa of the Periodic Table of the Elements; and R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> are each independently defined as hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, cycloalkyl and substituted cycloalkyl or R<sup>6</sup> is optionally a -(CR<sup>7</sup>R<sup>8</sup>)<sub>1</sub>- group linking two B when k is 2, wherein R<sup>7</sup> and R<sup>8</sup> are each independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, cycloalkyl, and substituted cycloalkyl, and l is an integer from 1 to 7; and

k is 1 when W is oxygen or sulfur and 2 when W is nitrogen.

- 27. The method of Claim 26, further comprising removing the protecting group (B-R<sup>4</sup>R<sup>5</sup>R<sup>6</sup>) to liberate W.
- 28. The method of Claim 27, further comprising reacting said liberated W with one or more comonomers to form a polymer segment.
  - 29. The method of Claim 28, wherein said comonomers are selected from the group consisting of cyclic ethers, diamines, diisocyanates, polyisocyanates, di-, poly- and cyclic amides, di- and polycarboxylic acids, diols, polyols, anhydrides, and mixtures thereof.

- 30. The method of Claim 27, further comprising reacting said liberated W with an agent containing a reactive olefinic bond to form an olefinic terminal group.
- 31. The method of Claim 30, wherein said agent is acryoyl or methacryoyl chloride.
- 5 32. The method of Claim 22, wherein:

said terminating step comprises reacting said living polymer with ethylene oxide; and

said treating step comprises treating said polymer under conditions sufficient to form an  $\alpha$ -olefin,  $\omega$ -olefin macromonomer.

- 10 33. The method of Claim 22, wherein said polymerization step comprises polymerizing one or more anionically polymerizable monomers selected from the group consisting of olefin monomers, alkenylsubstituted aromatic monomers, polar monomers and mixtures thereof.
  - 34. The method of Claim 33, wherein said anionically polymerizable monomer comprises one or more olefin monomers.
  - 35. The method of Claim 34, wherein said one or more olefin monomers comprises ethylene.
  - 36. The method of Claim 34, wherein said one or more olefin monomers comprises one or more conjugated diene monomers.
- 37. The method of Claim 36, wherein said one or more conjugated diene monomers is selected from the group consisting of 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, myrcene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-pentadiene, 1,3-hexadiene, 2-methyl-1,3-hexadiene, 1,3-heptadiene, 3-methyl-1,3-heptadiene, 1,3-octadiene, 3-butyl-1,3-octadiene, 3,4-dimethyl-1,3-hexadiene, 3-n-propyl-1,3-pentadiene, 4,5-diethyl-1,3-octadiene, 2,4-diethyl-1,3-butadiene, 2,3-di-n-propyl-1,3-butadiene, 2-methyl-3-isopropyl-1,3-butadiene, and mixtures thereof.

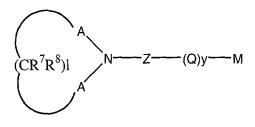
- 38. The method of Claim 37, wherein said one or conjugated diene monomers comprises butadiene.
- 39. The method of Claim 37, wherein said one or more conjugated diene monomers comprises isoprene.
- 5 40. The method of Claim 36, further comprising hydrogenating said polymer.
  - 41. The method of Claim 33, wherein said anionically polymerizable monomer comprises one or more alkenylsubstituted aromatic monomers.
- 42. The method of Claim 41, wherein said one or more alkenylsubstituted aromatic monomers comprises styrene, alpha-methylstyrene, vinyltoluene, 2-vinylpyridine, 4-vinylpyridine, 1-vinylnaphthalene, 2-vinylnaphthalene, 1-alpha-methylvinylnaphthalene, 2-alpha-methylvinylnaphthalene, 1,2-diphenyl-4-methyl-1-hexene, 3-methylstyrene, 3,5-diethylstyrene, 4-*tert*-butylstyrene, 2-ethyl-4-benzylstyrene, 4-phenylstyrene, 4-p-tolylstyrene, 2,4-divinyltoluene, 4,5-dimethyl-1-vinylnaphthalene, and mixtures thereof.
- 15 43. The method of Claim 42, wherein said one or more alkenylsubstituted aromatic monomers comprises styrene.
  - 44. The method of Claim 42, further comprising hydrogenating said polymer to form a polymer comprising vinylcyclohexane units.
- 45. The method of Claim 44, wherein said polymerization step comprises copolymerizing styrene and ethylene to form vinylcyclohexane-b-ethylene blocks.
  - 46. A method for making terminal olefin functionalized macromonomers, the methods comprising:

anionically polymerizing one or more monomers with at least one protected functionalized initiator of the formula:

$$(R^1R^2R^3-A)_2-N-Z-(Q)_y-M,$$

or

25



wherein:

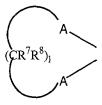
M is an alkali metal;

Z is a C3 to C18 linear, branched or cyclic alkylene radical, optionally containing aryl or substituted aryl groups;

Q is a hydrocarbyl group derived by incorporation of a compound selected from the group consisting of conjugated dienes, alkenylsubstituted aromatic compounds and mixtures thereof;

y is a number greater than 0 to about 5; and

10  $(A-R^1R^2R^3)$  and



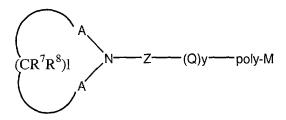
are protecting groups in which each A is independently an element selected from Group IVa of the Periodic Table of the Elements;  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^7$  and  $R^8$  are each independently defined as hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, cycloalkyl and substituted cycloalkyl; and l is an integer from 1 to 7;

to form at least one living polymer anion of the formula

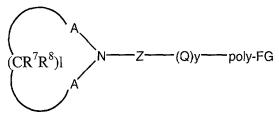
$$(R^1R^2R^3-A)_2-N-Z-(Q)_y$$
-poly-M

or

15



terminating polymerization to form at least one polymer of the formula  $(R^1R^2R^3-A)_2$ -N-Z- $(Q)_v$ -poly-FG or



wherein FG is hydrogen or a protected or unprotected functional group;

treating said protected tertiary amine group under conditions sufficient to provide a modified amine group capable of elimination; and

treating said polymer under conditions sufficient to eliminate the modified amine group to form a polymer having a terminal olefin group of the formula  $H_2C=CH-Z-(Q)_y$ -poly-FG.

- 10 47. The method of Claim 46, wherein said terminating step comprises an acid quenching step.
  - 48. The method of Claim 46, wherein said terminating step comprises reacting said living polymer with a functionalizing agent.
- 49. The method of Claim 48, wherein said functionalizing agent is selected from the group consisting of alkylene oxides; oxygen; sulfur; carbon dioxide; halogens; propargyl halides; alkenylhalosilanes; omega-alkenylarylhalosilanes; sulfonated compounds; amides; silicon acetals; 1,5-diazabicyclo[3.1.0]hexane; allyl halides; acryloyl and methacryloyl chloride; amines; epihalohydrins; and haloalkyl trialkoxysilanes.

50. The method of Claim 48, wherein said functionalizing agent is an electrophile of the structure:

$$X-Y-W-(B-R^4R^5R^6)_K$$

wherein:

5 X is halogen selected from chloride, bromide and iodide;

Y is a C1 to C18 linear, branched or cyclic alkylene radical, optionally containing aryl or substituted aryl groups;

W is oxygen, nitrogen or sulfur;

(B-R<sup>4</sup>R<sup>5</sup>R<sup>6</sup>) is a protecting group in which B is an element selected from Group IVa of the Periodic Table of the Elements; and R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> are each independently defined as hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, cycloalkyl and substituted cycloalkyl or R<sup>6</sup> is optionally a -(CR<sup>7</sup>R<sup>8</sup>)<sub>1</sub>- group linking two B when k is 2, wherein R<sup>7</sup> and R<sup>8</sup> are each independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, cycloalkyl, and substituted cycloalkyl, and l is an integer from 1 to 7; and

k is 1 when W is oxygen or sulfur and 2 when W is nitrogen.

- 51. The method of Claim 50, further comprising removing the protecting group (B-R<sup>4</sup>R<sup>5</sup>R<sup>6</sup>) to liberate W.
- 52. The method of Claim 51, further comprising reacting said liberated W with one or more comonomers to form a polymer segment.
  - 53. The method of Claim 52, wherein said comonomers are selected from the group consisting of cyclic ethers, diamines, diisocyanates, polyisocyanates, di-, poly- and cyclic amides, di- and polycarboxylic acids, diols, polyols, anhydrides, and mixtures thereof.
- 25 54. The method of Claim 51, further comprising reacting said liberated W with an agent containing a reactive olefinic bond to form a olefinic terminal group.
  - 55. The method of Claim 54, wherein said agent is acryoyl or methacryoyl chloride.

56. The method of Claim 46, wherein:

said terminating step comprises reacting said living polymer with ethylene oxide; and

said treating step comprises treating said polymer under conditions sufficient to form an  $\alpha$ -olefin,  $\omega$ -olefin macromonomer.

- 57. The method of Claim 46, wherein said polymerization step comprises polymerizing one or more anionically polymerizable monomers selected from the group consisting of olefin monomers, alkenylsubstituted aromatic monomers, polar monomers and mixtures thereof.
- 10 58. The method of Claim 57, wherein said anionically polymerizable monomer comprises one or more olefin monomers.
  - 59. The method of Claim 58, wherein said one or more olefin monomers comprises ethylene.
- 60. The method of Claim 58, wherein said one or more olefin monomers comprises one or more conjugated diene monomers.
  - 61. The method of Claim 60, wherein said one or more conjugated diene monomers is selected from the group consisting of 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, myrcene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-pentadiene, 1,3-hexadiene, 2-methyl-1,3-hexadiene, 1,3-hexadiene, 3-methyl-1,3-heptadiene, 1,3-octadiene, 3-butyl-1,3-octadiene, 3,4-dimethyl-1,3-hexadiene, 3-n-propyl-1,3-pentadiene, 4,5-diethyl-1,3-octadiene, 2,4-diethyl-1,3-butadiene, 2,3-di-n-propyl-1,3-butadiene, 2-methyl-3-isopropyl-1,3-butadiene, and mixtures thereof.
  - 62. The method of Claim 61, wherein said one or conjugated diene monomers comprises butadiene.
- 25 63. The method of Claim 61, wherein said one or more conjugated diene monomers comprises isoprene.
  - 64. The method of Claim 60, further comprising hydrogenating said polymer.

- 65. The method of Claim 57, wherein said anionically polymerizable monomer comprises one or more alkenylsubstituted aromatic monomers.
- 66. The method of Claim 65, wherein said one or more alkenylsubstituted aromatic monomers comprises styrene, alpha-methylstyrene, vinyltoluene, 2-vinylpyridine, 4-vinylpyridine, 1-vinylnaphthalene, 2-vinylnaphthalene, 1-alpha-methylvinylnaphthalene, 2-alpha-methylvinylnaphthalene, 1,2-diphenyl-4-methyl-1-hexene, 3-methylstyrene, 3,5-diethylstyrene, 4-tert-butylstyrene, 2-ethyl-4-benzylstyrene, 4-phenylstyrene, 4-p-tolylstyrene, 2,4-divinyltoluene, 4,5-dimethyl-1-vinylnaphthalene, and mixtures thereof.
- 10 67. The method of Claim 66, wherein said one or more alkenylsubstituted aromatic monomers comprises styrene.
  - 68. The method of Claim 67, further comprising hydrogenating said polymer to form a polymer comprising vinylcyclohexane units.
- 69. The method of Claim 68, wherein said polymerization step comprises copolymerizing styrene and ethylene to form vinylcyclohexane-b-ethylene blocks.
  - 70. The method of Claim 46, wherein treating said protected tertiary amine to provide a modified amine group capable of elimination comprises reacting said protected tertiary amine group with a quaternizing agent to form a quaternary amine group.
- 71. The method of Claim 70, wherein treating said polymer to eliminate said modified amine group comprises heating said polymer.
  - 72. The method of Claim 46, wherein treating said protected tertiary amine to provide a modified amine group capable of elimination comprises reacting said protected tertiary amine group with a peroxide or peracid to form an N-oxide group.
- 73. The method Claim 72, wherein treating said polymer to eliminate said modified amine group comprises heating said polymer.

- 74. The method of Claim 22, wherein said treating step to eliminate the hydroxyl group to form a polymer having a terminal olefin group comprises dehydrating said polymer using a hydroxyl dehydrating agent.
- 75. The method of Claim 74, wherein said hydroxyl dehydrating agent is selected from the group consisting of H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, metallic oxides, sulfides, metallic salts, zeolites, P<sub>2</sub>O<sub>5</sub>, I<sub>2</sub>, ZnCl<sub>2</sub>, BF<sub>3</sub>-etherate, dimethyl sulfoxide, KHSO<sub>4</sub>, and phthalic anhydride.
  - 76. The method of Claim 74, wherein said dehydrating agent is an acid dehydrating agent.
- The method of Claim 76, wherein said acid dehydrating agent is H<sub>2</sub>SO<sub>4</sub>
  - 78. The method of Claim 76, wherein said acid dehydrating agent is H<sub>3</sub>PO<sub>4</sub>.
  - 79. The method of Claim 74, wherein said treating step is conducted at a temperature of at least about 100°C.